

Sulfuric Acid in the Icy Crust of Europa

R. W. Carlson^{1*}, R. E. Johnson², M. S. Anderson¹

¹ Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109

² Engineering Physics, University of Virginia, Charlottesville, VA 22903-2442

*To whom correspondence should be addressed at Mail Stop 183-601, Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena CA 91109. E-mail: rcarlson@lively.jpl.nasa.gov

Abstract

Infrared spectra of Europa's surface obtained by the Galileo spacecraft show hydrated compounds identified here as sulfuric acid octahydrate and sulfuric acid hemihexahydrate. In addition, Europa's visually dark material, which spatially correlates with the concentration of hydrate, is identified as radiolytically altered sulfur polymers. We propose that radiolysis rapidly and continuously recycles sulfur between three forms: sulfuric acid, sulfur dioxide, and sulfur polymers, with sulfuric acid observed to be about 50 times more abundant than the other forms.

Europa is unique among Jupiter's moons. It is not only differentiated (1), with an ice crust that is subject to tidal heating (2), but melting may occur, producing a subsurface ocean (2, 3). The surface may be young and possibly renewed by solid state convection (4) or extrusions of solid or liquid material from below (5). The surface is also subject to intense bombardment by high-energy electrons, protons, and ions of sulfur and oxygen (6, 7, 8). These particles can alter the surface through radiolysis (9, 10) and supply sulfur by implantation (11, 12).

Europa's surface exhibits bright, icy plains and darker, mottled terrain (5). Linear features with various morphologies crisscross the surface. These long, narrow features often show bright central bands flanked by bands of darker material ("triple bands"). Europa exhibits three visual-color components, two corresponding to ice with different grain sizes and the third being the darker, redder material (13). The leading hemisphere is icier, while the trailing side contains more dark material, predominantly in the mottled terrain.

The composition of a surface can provide information about formation processes. Europa's surface contains minor amounts of SO_2 , CO_2 , and H_2O_2 (10, 11, 14). The major species observed are water ice and hydrated materials (15, 16). Evidence for hydration – the chemical combination with H_2O in which the H_2O molecule retains its molecular state – is found by shifts and distortions of H_2O absorption bands that occur from chemical binding. For example, the $2.0\text{-}\mu\text{m}$ H_2O band (stretch + bending vibration transition) is symmetric in ice spectra, but becomes asymmetric when H_2O is bonded to another molecule and the force field changes. Other H_2O bands are similarly affected by hydration. Europa spectra (Fig. 1A) obtained by Galileo's near

infrared mapping spectrometer (NIMS), vary between two extremes (end-members), from ice-like, with a symmetric 2- μm band, to predominately hydrated, with highly distorted H_2O bands. Most NIMS spectra of Europa indicate mixtures of these two end-members. Although the hydrate is ubiquitous on Europa, there is more on the trailing hemisphere and within the linear features and dark mottled terrain. (16).

It has been suggested (16) that these bands are due to hydrated salt minerals (Fig. 1B) such as epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), magnesium hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), natron ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) and others. This hypothesis requires combining spectra of several salts. It was suggested as providing evidence for a subsurface ocean (16) with salt minerals being formed on Europa's surface (17) by extrusion of subsurface brine that evaporate to form salt pans, similar to terrestrial deposits. However, identification of specific hydrates is not unique.

The occurrence of H_2O_2 and SO_2 in the icy surface of Europa suggested to us the formation of sulfuric acid (H_2SO_4), a common photochemical product in the atmospheres of Earth and Venus. We show that NIMS IR spectra of Europa are consistent with the presence of hydrated H_2SO_4 and that its occurrence in Europa's surface is a consequence of radiolysis.

Frozen H_2SO_4 hydrates occur as amorphous or crystalline $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ where $n = 1, 2, 3, 4, 6.5,$ and 8 . (18, 19, 20). We investigated the $n = 4, 6.5, 8$ hydrates by freezing stoichiometric solutions and obtaining their IR reflectance spectra. The samples were largely amorphous (preparation of $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ crystals requires repeated cycles of freezing and partial melting)

(20). We used spectrally neutral diamond powder to produce a diffusely reflecting medium containing $\text{H}_2\text{SO}_4 \bullet n\text{H}_2\text{O}$ grains. Spectra were obtained for $\text{H}_2\text{SO}_4 \bullet 8\text{H}_2\text{O}$ for various grain sizes and temperatures between ~ 80 K and the melting point (~ 220 K). The laboratory spectra (Fig. 1C) of $\text{H}_2\text{SO}_4 \bullet 6.5\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \bullet 8\text{H}_2\text{O}$ are similar, and show little variation with temperature. Spectra of the tetrahydrate H_2O bands were found to be less distinct and unlike those in Europa's spectra. A Europa hydrate spectrum compared with a laboratory $\text{H}_2\text{SO}_4 \bullet 8\text{H}_2\text{O}$ spectrum shows agreement (Fig. 1D), and provides the best match yet found for any single compound. There are similarities in the shapes of the H_2O bands, the common presence of a broadened $1.25\text{-}\mu\text{m}$ H_2O band, and similar absorption at $1.8\text{ }\mu\text{m}$.

The small differences between the Europa and laboratory spectra (Fig. 1D) may be due to several effects. (a) The Europa spectrum also contains ice features. This will produce the $1.04\text{-}\mu\text{m}$ H_2O band, enhance the $1.25\text{-}\mu\text{m}$ H_2O band, provide more absorption in the $2.5\text{-}\mu\text{m}$ region, and enhance the relative reflectivity between $1.6\text{ }\mu\text{m}$ to $1.8\text{ }\mu\text{m}$. (b) Other hydrates may also be present. (c) The wavelengths of absorption minima of hydrates are reduced by ion irradiation, possibly due to disruption of the structure or dehydration. Shifts of $\sim 0.02\text{ }\mu\text{m}$ were produced in the spectra of hydrates irradiated by protons (21) and may be responsible for the small mismatch between the wavelengths of band minima found in the Europa and laboratory spectra. (d) The laboratory spectra may have a small offset, caused by reflection from diamond particles at the surface. This effect artificially suppresses the contrast in band absorption profiles and may cause

whose spectra are consistent with hydrated H_2SO_4 (29). Radiolysis of pure SO_2 ice produces sulfur, sulfate, and (predominately) SO_3 (30). In the presence of water, SO_3 rapidly forms H_2SO_4 in an exothermic reaction (31). The G -value for SO_2 in H_2O ice is not available so we use the value for SO_3 production in pure SO_2 ice ($G \sim 5$) (30). With this G value, Europa's SO_2 concentration, and using $\sim 5 \times 10^{10} \text{ keV s}^{-1} \text{ cm}^{-2}$ for Europa's irradiation flux (8), we obtain an H_2SO_4 production of $\sim 1 \times 10^9 \text{ s}^{-1} \text{ cm}^{-2}$. Irradiation of polymerized S in H_2O ice and associative reactions of SO_2 with H_2O_2 can also produce H_2SO_4 , so the above rate is a lower limit. The optically observed amount of H_2SO_4 can be formed from SO_2 and polymerized S in $< 10^4$ years.

Sulfuric acid is quite stable under irradiation. When H is removed from H_2SO_4 it recombines quickly (32). Destruction of SO_4 is moderated by radiation-induced reactions between SO_2 and H_2O_2 (33). The net destruction rate can be estimated from rates for another acid sulfate, Li_2SO_4 , which exhibits $G \sim 10^{-3}$ to 10^{-4} when in concentrated form. These values are consistent with upper limits for H_2SO_4 at Europa's concentration levels (33). The high radiation stability of H_2SO_4 implies large H_2SO_4 concentrations, compared to SO_2 and polymerized S. This finding agrees with our observation that Europa's H_2SO_4 is more abundant than either SO_2 or polymerized S by about a factor of 100 (assuming that the photon sampling depths are about the same). The G -values, for X-ray and γ -ray irradiation, give lower bounds for destruction by energetic particles, $\sim 5 \times 10^7$ to $5 \times 10^8 \text{ s}^{-1} \text{ cm}^{-2}$. Heavy ions and UV radiation, both having smaller penetration depths, can also decompose H_2SO_4 , but G -values and cross-sections are not available.

Although equilibrium between the three chemical forms is established rapidly, there can be a longer term net imbalance leading to the suggested brightening of surfaces with age (34), such as from the a slow net oxidation of the polymerized S reservoir due to loss of H and transport of SO₂ by sputtering.

The sulfur that produces H₂SO₄, SO₂, and polymerized S may have been originally implanted from the jovian plasma. The current influx, $\sim 6 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ (7), provides sufficient sulfur to account for the three reservoirs in 10⁴ years. If this were the only currently active source one would expect a more uniform distribution of H₂SO₄ hydrate and dark material. Some geological process or endogenic source has produced a non-uniform distribution of sulfurous material. For example, deposits of extruded evaporite salts, if present, may provide sulfate. In this case, implanted protons may replace salt mineral cations to form H₂SO₄. Radiolysis of evaporite salt minerals should also produce MgO, MgOH, Mg(OH)₂ (brucite), Na₂O, and NaOH (17, 35). However, brucite exhibits a sharp OH band at 1.4 μm (36) that is not evident in NIMS spectra (Fig. 1A).

Another possibility is burial of previously implanted sulfur, reappearing on the surface due to geological processes. For example, solid state convection or impact gardening can bury surface material, forming a crust enriched with sulfur compounds. Cracks in the crust can be filled by extrusion of ice or liquid water from below. This upwelling material can scour the crack walls, forming two layers of upward moving sulfurous till. The surface expression would be two dark

bands and possibly a bright median of pure ice, similar to the appearance of Europa's triple bands (5).

The melting point of sulfuric acid solutions can be as much as 55 K lower than that of pure water ice (18), so with sufficient H_2SO_4 production and burial, a subsurface layer of liquid sulfuric acid may be formed. This layer could provide a low viscosity boundary for crustal motion. Sulfuric acid can supercool to 150 K (19), possibly facilitating cryovolcanic activity. The acid is also an electrical conductor and may contribute to Europa's magnetic perturbation (37). Because the surfaces of Ganymede and Callisto contain SO_2 and H_2O they are likely to contain H_2SO_4 hydrate.

References and notes

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FIGURE CAPTIONS

Fig. 1. IR Reflectance spectra of Europa and candidate surface materials. (A) NIMS Europa end-member spectra, with ice \gg hydrate (—) and hydrate \gg ice (—•—). (B) Evaporite salt minerals (16). (C) Spectra of $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$ for various n , grain size d , and temperature T : $n = 8$, $d = 5 \mu\text{m}$, $T = 80 \text{ K}$, offset by 0.10 (— — —); $n = 8$, $d = 50 \mu\text{m}$, 80 K , offset by 0.05 (— — —); $n = 8$, $d = 50$, $T = 140 \text{ K}$ (—); $n = 6.5$, $d = 50 \mu\text{m}$, $T = 80 \text{ K}$ (••••••). (D) Comparison of Europa hydrate spectrum (—•—, from A) and $\text{H}_2\text{SO}_4 \cdot 8\text{H}_2\text{O}$ at $T = 140 \text{ K}$, $d = 50 \mu\text{m}$, normalized at $1.1 \mu\text{m}$ (—, from C). Differences between the two are discussed in the text.

Fig. 2. Reflectance spectra of Europa's trailing side compared to photolyzed and radiolyzed sulfur compounds. Europa spectrum (24) (•••••); Photolyzed $\text{H}_2\text{S} + 10 \text{ H}_2\text{O}$ (27) (—); Transmission of ion irradiated SO_2 (26), assumed here to approximate the reflectance when the same number of molecules are in the optical path (••••••); SO_2^+ irradiated H_2O ice (25), assumed to be equivalent to implanted and irradiated S (—♦—).

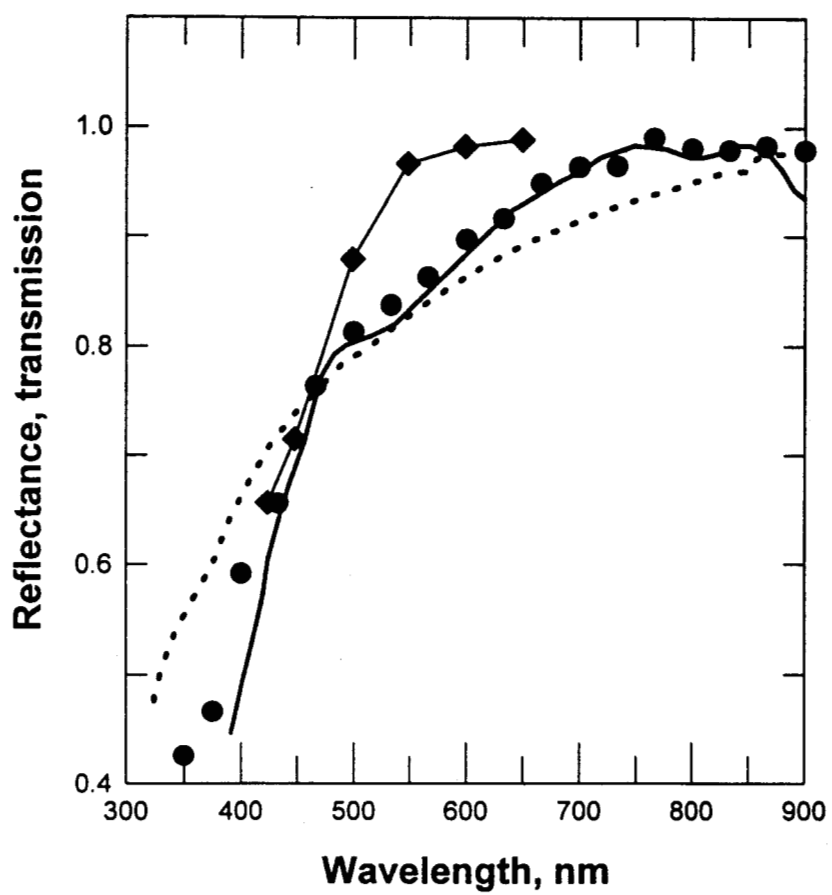


Fig. 2

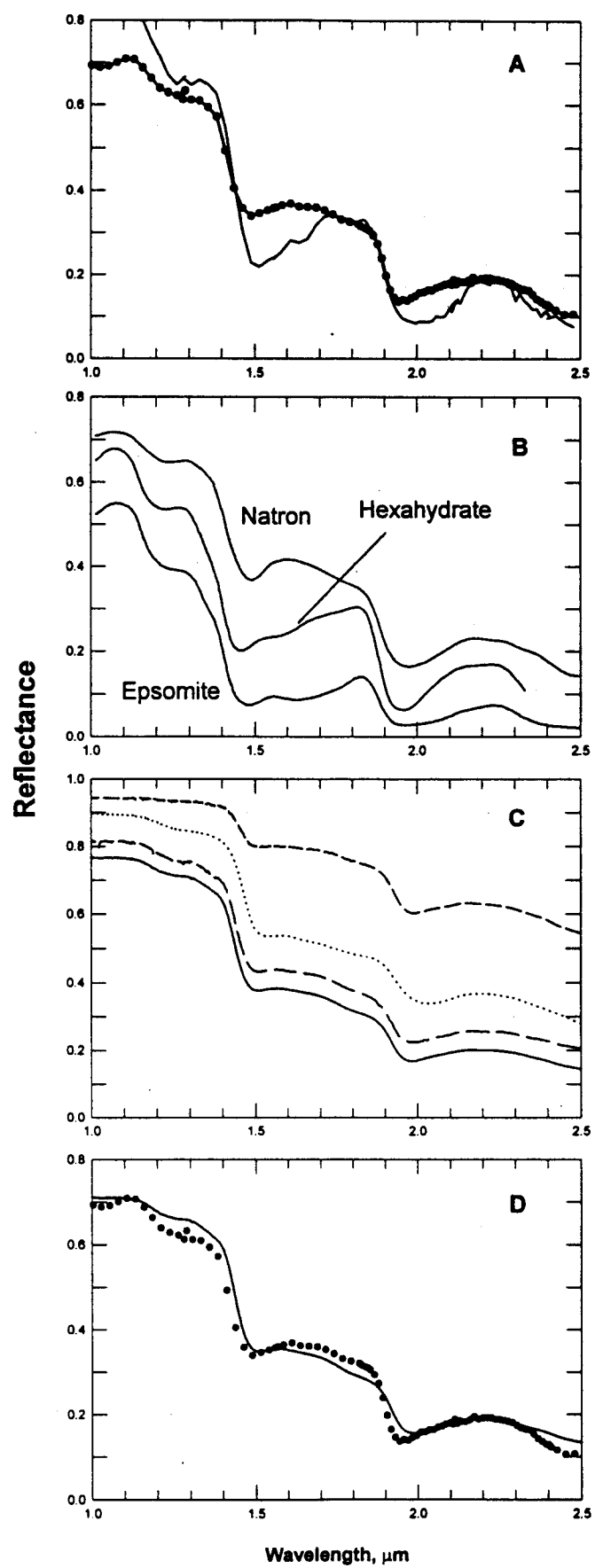


Fig. 1